

MINERAL ASSOCIATIONS IN PULVERIZED COAL

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INTRODUCTION

Ash formed during the combustion of pulverized coal produces a variety of operational and environmental problems. Efforts to anticipate and control these problems have led to the development of mathematical models to predict mineral transformations and deposition during combustion of pulverized coal. These models require a description of the coal mineral matter as input. Advanced analytical techniques such as Computer Controlled Scanning Electron Microscopy (CCSEM) have been developed to provide the required information.

Early development of the CCSEM technique was performed by Huggins *et al.* [1] who used a scanning electron microscope equipped with a Tracor Northern 2200 X-ray analysis system to examine coal minerals. The Energy and Environmental Research Center at the University of North Dakota has developed and refined the technique for both coal minerals and ash [2]. Additional work on the association of the coal minerals with the organic matrix has been performed by Straszheim and co-workers at Iowa State University with use of a sophisticated image analysis system (LeMont Scientific DB-10) [3]. Recent work in our laboratory has examined mineral/mineral associations in coal particles [4]. This paper contains a brief description of the associations of two key minerals from two eastern U.S. bituminous coals.

ANALYSIS PROCEDURE

Computer Controlled Scanning Electron Microscopy was performed with use of a JSM-840A scanning electron microscope (JEOL) equipped with an eXL-FQAI Microanalysis System (Oxford Analytical), a Pentafet LZ5 Light Element Detector (Oxford), a LEMAS Stage Automation System (Oxford) and an ultra-thin window (MOXTEK). Samples were mounted with a mixture of carnauba wax and Cerita wax (M. Argueso & Co., Inc., Mamaroneck, NY) [5]. Carnauba wax was chosen to provide sufficient contrast between the coal and the mounting material on the backscattered electron image [6]. The Cerita wax was used to decrease sample cracking. Mounted samples were sectioned, polished, and coated with carbon.

The description of the analysis procedure which follows has been presented elsewhere and is repeated here for completeness [4]. Two automated analysis routines, Quantitative Mineral Analysis (QMA) and Analysis of Mineral and Coal Associations (AMCA), were developed. QMA was used to determine the size and composition of mineral particles by analyzing samples at magnifications of 100X and 400X. During the analysis, the sample stage was moved to predefined positions or fields where a backscattered electron image was collected. For each field, the sizes and positions of mineral particles were determined and stored. The electron beam was then moved to the center of each mineral particle and an X-ray spectrum was collected for 2 seconds (approximately 10,000 X-ray counts). Next, peak and background corrections were made. A ZAF correction was then made to account for the effects of atomic number (Z), absorption (A), and fluorescence (F) at each analysis point. The composition in weight percent was subsequently stored and the beam was moved to the next mineral particle for analysis. After analysis of all the particles in a given field, the stage was moved to the next field and the process was repeated. The results from both magnifications were then classified to identify the mineral species present, and combined off-line on a Sun computer workstation. A typical QMA analysis required approximately 12 hours of beam time to analyze 3000 to 4000 mineral particles.

The AMCA routine combined the quantitative mineral analysis with image analysis to determine the association of minerals with the coal matrix. This analysis was similar to the mineral-only analysis except that the backscattered electron images were also saved during the analysis, and the samples were analyzed at a single magnification of 220X. The stored images were later processed with use of Mineral Liberation image analysis software on the eXL, and the mounting medium, coal and minerals were identified by their respective brightness on the backscattered electron image. The amount (area) of coal and/or minerals on each particle, as well as the particle size and location were determined and stored. This information was then combined with the composition data on the mineral particles to yield the particle-by-particle mineral content for the coal. A typical AMCA analysis included about 35,000 coal and mineral particles and required approximately 24 hours of beam time in addition to off-line processing.

These procedures were used to examine two eastern U.S. bituminous coals which were recently tested in a utility boiler [7]. Ultimate and proximate analyses of these two coals are given in Table 1 [8].

RESULTS AND DISCUSSION

Table 2 shows the major mineral matter species found in the coal as determined with the QMA procedure. The weight fraction of each species was approximated from the measured area fraction with use of the species density by assuming that the volume fraction was equivalent to the area fraction [9]. As seen from the data, Coal A has significantly more pyrite than Coal B. On the other hand, Coal B has more K-Al-Silicates and more aluminosilicates than Coal A. Both pyrite and K-Al-Silicates have been identified as species which may contribute to slagging problems in boilers.

Data on the mineral content of the individual particles from AMCA were used to examine the association of specific minerals in the coal. Associations were determined by identifying particles which contained either pyrite or K-Al-Silicate minerals and then evaluating, on a frequency basis, other minerals also contained in that particle. Note that the sum of the percent association over all minerals may be greater than 100 percent since a single mineral grain may be associated with several other types of grains in the same coal particle.

Figures 1 and 2 provide association data for K-Al-Silicate and pyrite, respectively. The extent of association for the K-Al-Silicates, including the lack of association with pyrite, was similar to that of other silica-bearing minerals. In contrast, the pyrite shows a large percentage of "self-association" (i.e., pyrite present in particles with no other minerals). Analysis of the individual pyrite particles showed that 69% of the self-associated pyrite in Coal A and 57% in Coal B was present in particles which contained less than 80% mineral (area basis). In fact, a substantial fraction (31% of the self-associated pyrite in Coal A and 21% in Coal B) was found in particles containing less than 20% mineral. These data indicate that pyrite in these two coals does not tend to associate as extensively as the K-Al-Silicate minerals, and that a significant fraction (by number) of the pyrite was included or locked in the coal matrix of particles where pyrite was the only mineral present.

Results for self-associated K-Al-Silicates showed that 47% in Coal A and 27% in Coal B were present in particles which had less than 20% mineral. In other words, almost half of the K-Al-Silicate minerals in Coal A which were not associated with other minerals were included in coal particles that contained less than 20% mineral. Clearly, the fact that a mineral is self-associated does not imply that it is excluded.

Some interesting differences between the two coals can be seen in Figure 1. A higher fraction of K-Al-Silicate minerals in Coal B were self-associated. Also, a significantly lower percentage of K-Al-Silicates in Coal B were associated with quartz. A mixture of K-Al-Silicates with quartz would probably have a higher melting point than the K-Al-Silicate alone. The association of K-Al-Silicates with aluminosilicates was also lower in Coal B, in spite of the fact that Coal B contained a much higher percentage (by weight) of aluminosilicates. Coal B also contained more ash and had a higher weight percent of K-Al-Silicates in the ash (see Tables 1 and 2). Therefore, a boiler

burning Coal B may be more likely to experience deposition problems associated with K-Al-Silicate minerals which typically melt under normal combustion conditions [10].

Mineral/mineral associations were also examined as a function of the size of the mineral grains. Intuitively, one might expect larger particles to be excluded and show lower levels of association, while the smaller particles are included or locked in the coal matrix. Figure 3 shows the fraction of pyrite that was self-associated as a function of mineral size for Coal B. Included in each bar is the percent of the self-associated minerals that were excluded (i.e., in particles with greater than 80% mineral). The majority of small pyrite grains were not associated with other minerals. A large fraction of these small grains (41%) was also excluded. It is possible that fragmentation of the large excluded pyrite particles during pulverizing was responsible for the presence of small excluded pyrite grains. The fraction of pyrite associated with other minerals was lowest for the larger pyrite particles.

The data for K-Al-Silicate particles were somewhat different as shown in Figure 3. The level of self-association was lower than that observed for pyrite. The level of self-association decreased with increasing mineral particle size. No self-associated K-Al-Silicate particles were found in the large size range. The percentage of the self-associated particles which were also excluded was significantly lower for the K-Al-Silicate minerals than for pyrite. Note that the size and morphology of ash formed from K-Al-Silicate minerals included in the coal matrix will probably be affected by the combustion behavior of the char (e.g. swelling vs. non-swelling).

Although the measurements and analysis presented in this paper provide insight into coal/mineral and mineral/mineral associations, the results are not without limitations. For example, the association data is based on two-dimensional cross-sections of particles which may underestimate the degree of association. The importance of this effect is currently under investigation. Also, there is a limit on the size of particle for which a reasonable composition may be obtained. Thus, the mineral data do not reflect the presence of small mineral inclusions less than about 1 micron in diameter. The statistical validity of large particle data is a problem for samples where only a few large particles are present. While these limitations may affect the magnitude of the results, they are not expected to change the significance of the key observations presented in this paper.

CONCLUSIONS

Computer Controlled Scanning Electron Microscopy has been implemented on a JEOL 840A scanning electron microscope equipped with an Oxford eXL X-ray microanalysis and image analysis system. This system was used to analyze the mineral composition of two eastern U.S. bituminous coals. In addition, a procedure was developed to determine the association of the minerals with the coal matrix and with other minerals within the coal. The mineral content of each coal was determined on a particle-by-particle basis and used to examine the association of both pyrite and K-Al-Silicate minerals in the coal. Results showed differences in the association of each of these two minerals for both of the coals analyzed.

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Table 1. Properties of Coals A and B [10].

Proximate Analysis				
	Coal A		Coal B	
	% as received	% dry	% as received	% dry
Moisture	4.9	---	6.15	---
Ash	7.4	7.6	10.4	11.5
Volatile	34.95	37.25	18.75	19.40
Sulfur	2.01	2.0	1.41	1.50
Heating Value (kJ/kg)	31,249	32,714	30,470	32,123
Ultimate Analysis (%)				
	Coal A		Coal B	
Carbon	77.0	81.8	73.5	78.0
Hydrogen	3.69	3.89	4.2	4.35
Nitrogen	1.22	1.29	1.10	1.17
Oxygen	3.85	4.05	3.00	3.5
Ash Fusion Temperature Data (K)				
	Coal A		Coal B	
	Reducing Atmosphere	Oxidizing Atmosphere	Reducing Atmosphere	Oxidizing Atmosphere
Initial	2080	2310	2770	>2800
Deformation				
Softening	2175	2400	>2800	>2800
Hemispherical	2245	2460	>2800	>2800
Fluid	2295	2500	>2800	>2800

Table 2. Mineral particle size and composition distributions (% by weight).

Major Mineral Phases	% of Total Mineral Coal A	% of Total Mineral Coal B
Quartz	8.7	5.3
Fe ₂ O ₃ /FeCO ₃	1.3	1.2
Aluminosilicate	38.1	54.4
Ca-Al-Silicate	0.9	0.7
Fe-Al-Silicate	0.7	0.7
K-Al-Silicate	11.5	17.8
Pyrite	30.4	14.8
CaCO ₃ /CaO	3.4	0.5
Unknown	3.1	3.3
Total	100.0	100.0

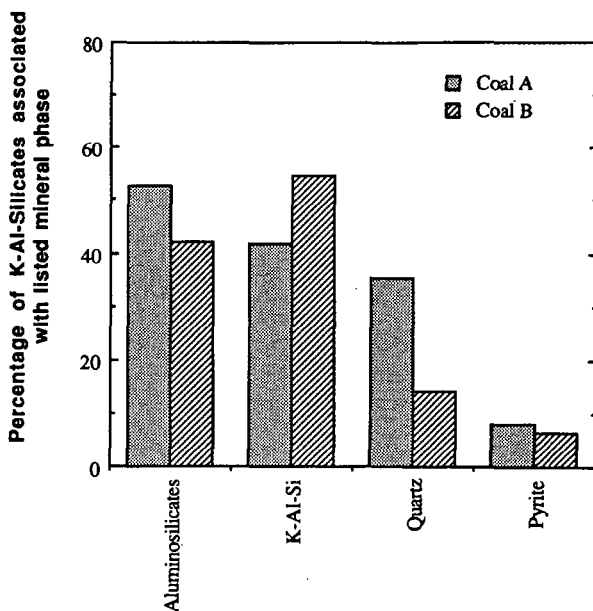


Figure 1. Association of K-Al-Silicates with other major coal minerals phases.

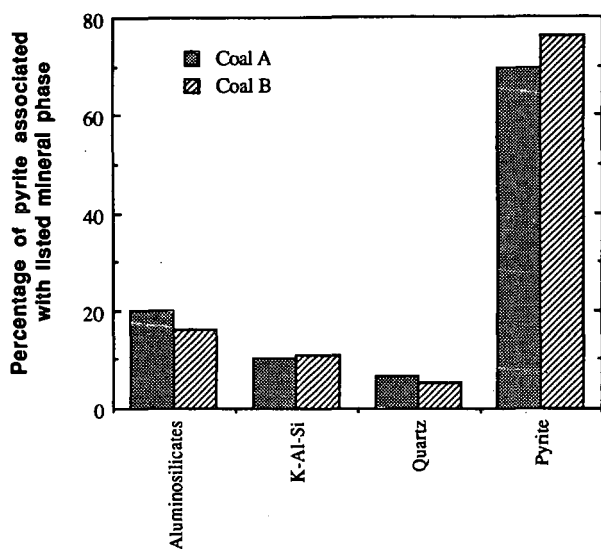


Figure 2. Association of pyrite with other major coal mineral phases.

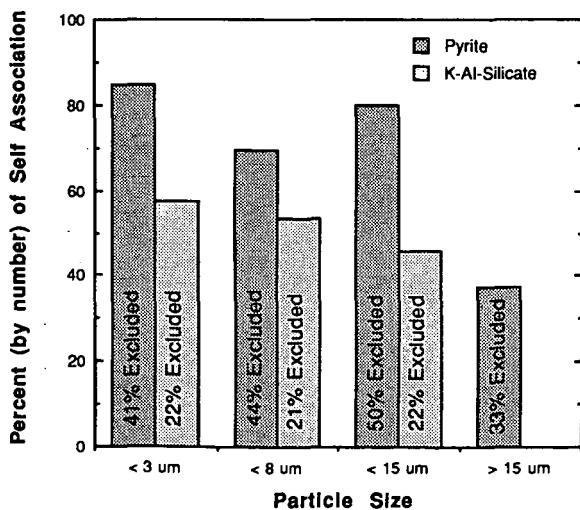


Figure 3. Extent of self-association and the percent of self-associated particles which were excluded as a function of the mineral grain size.